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Electronic States near Dislocations in Transition Metals: An Application of Quantum Chemistry in Technology

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Abstract

This paper outlines a model for calculating the localized states of a ⟨100⟩ edge dislocation in α-Fe. The model used for the calculations is based on the multiple-scattering model (SCF-Xα-SW). The purpose of this research is twofold: (1) To determine changes in electronic structure of the lattice near the core region of defects in α-Fe. (2) The variations of hydrostatic pressure about an edge dislocation produce a rearrangement of the conduction electrons. The question is what electrical interaction might be expected between a dislocation and a charged solute atom. The calculations show that the electrons tend to flow away from the compression side toward the dilated regions. The electrical contribution to the binding energy of a solute atom and a dislocation in α-Fe is of the order of 0.01 Ry/electronic unit charge of the atom.

1. Introduction

The scattering of the conduction electrons by dislocations in solids has proved to be a puzzling theoretical problem for nearly three decades. In the past, most of the investigations concerning the electronic states of dislocations were carried out for semiconductors. The quantum-mechanical consideration of such a complex system as a dislocation has been treated on the basis of more or less drastically simplified models. The problem is complicated because of the nature of the atomic configurations of crystal dislocations. Nevertheless, a realistic description of the atomic configuration in the vicinity of dislocations is essential for an understanding of the influence of the rearrangement of the conduction electrons about dislocations on plastic deformation. In particular, the electric field due to the conduction electrons affects the nature of the interaction between dislocations and impurities, which plays an important role in physical problems derived from materials science.

The present contribution is a sequel to a previous investigation on localized electronic states of a ⟨100⟩ edge dislocation in Mo [1–3]. Earlier work was focussed on the influence of the atomic positions on the electronic structure calculated. The purpose of the present investigation is twofold:

(1) To determine changes in electronic structure of the lattice near the core region of defects where local changes in symmetry occur. How much does the

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electronic structure shift when one approaches a line defect in α-Fe from far away in the perfect region?

(2) The variations of hydrostatic pressure about an edge dislocation produce a rearrangement of the conduction electrons, giving rise to an electric dipole. The field of this dipole can act on the nuclear charge of an impurity atom. The question is: how much is the contribution of that electronic component to the total interaction energy between dislocations and impurities?

The model used for the calculations of the electronic structure is based on the multiple-scattering model, suggested by Slater [4] and further developed by Johnson [5]. This model has been extensively discussed in a review by Johnson [6] and thoroughly documented in other publications [7,8], so that there is no need to describe the procedure in much detail here. In addition, the computer simulation procedure for calculating the atomic configuration of dislocations is combined with classical elasticity theory and the self-consistent scattered-wave model [3].

2. ⟨100⟩ Edge Dislocation in α-Fe

A simple dislocation with ⟨100⟩Burgers vector on a {100} slip plane in α-Fe is chosen because of the relatively high symmetry, necessary in connection with reduction of the eigenvalue problem yielding the electronic states. In the following we summarize briefly the method of the calculation employed in the dislocation model.

Approximately 3500 atoms are arranged in a body-centered-cubic (BCC) crystallographic configuration and embedded in an elastic continuum. The perfect ⟨100⟩ edge dislocation is introduced by removing two {100} half planes. In order to conserve the initial mirror symmetry, the third half plane is shifted over a distance $\frac{1}{2}\langle 100\rangle$. The initial positions of the atoms are obtained assuming anisotropic elasticity theory. The displacements for this system are given in Ref. 3. The step-by-step procedure for the construction of an edge dislocation is illustrated in Figure 1.

Once these initial atomic positions have been determined, it is assumed that they will relax to their final position under the influence of the assumed central atomic interaction function. For determining the displacements from the initial to the final positions, the equations of motion resulting from Newtonian mechanics are solved. The Johnson-I potential is used for the interatomic interaction function [10]. The relaxed configuration was found as depicted in Figure 2. Because of the symmetry along the dislocation line in the [001] direction, only seven atoms within the core are depicted. The atomic configuration thus obtained provides the necessary input of the atomic positions around the core region for the cluster calculations.

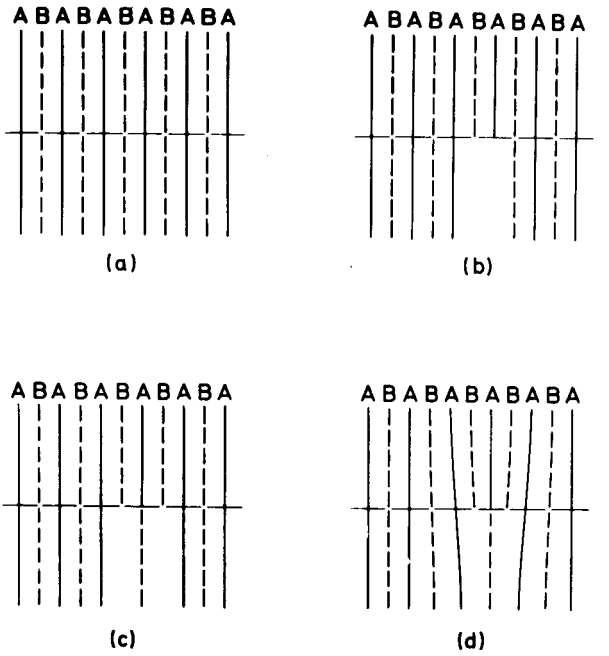

Figure 1. Step-by-step procedure for the construction of an edge dislocation: (a) perfect lattice; (b) removal of two half planes; (c) shifting one half plane B; (d) configuration (c) relaxed under continuum conditions.

3. Self-Consistent-Field Scattered-Wave Calculations

A. Perfect Lattice of α-Fe

The point group O_h is utilized for reduction of the eigenvalue problem. The cluster of one unit cell contains nine Fe atoms. A maximum l value of 2 was used for the decomposition of the wave function into spherical harmonics. Consequently, 81 functions have to be distributed over the irreducible representation in the O_h symmetry group. In the case of a cluster of nine Fe atoms, 72 electrons from the valence band have to be distributed over the irreducible representations.

In the present work the "muffin-tin" approximation was applied. The muffin-tin radius was chosen to be equal to 2.346 a.u. The charge density at each point of a cluster of atoms has been calculated using a computer program developed by Liberman et al. [11]. The Watson sphere radius was chosen to be 7.4 a.u. This value is slightly greater than the smallest value of the sphere enclosing the atoms, which is 7.1 a.u., but for comparison the orbital energies calculated for a perfect system with those of the dislocated system, equal values of the Watson radii were taken. The charge on the Watson sphere is zero. For a discussion of the Watson sphere see Refs. 1, 3, and 6.

For the ferromagnetic state, the results of the spin-polarized self-consistent

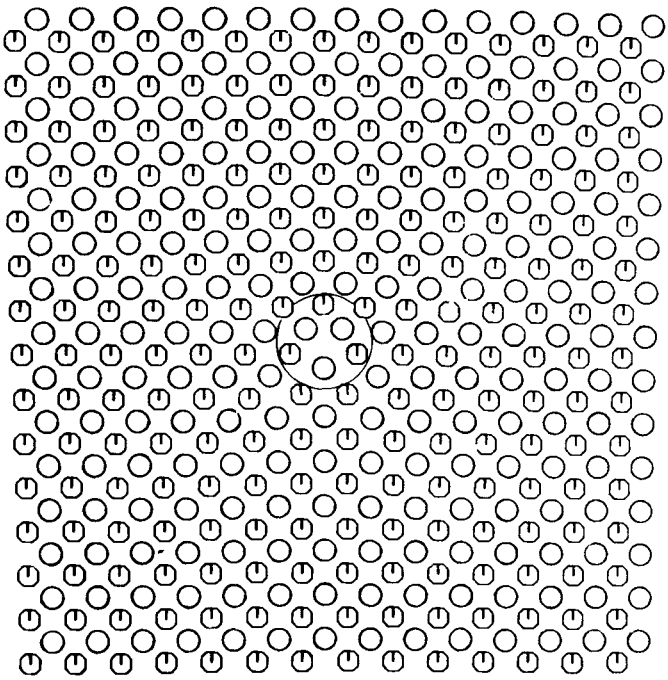

Figure 2. Two atomic layers projected on the (001) plane of the atomic configuration of a [100] edge dislocation in α-Fe.

calculation are summarized in Figure 3. In the ferromagnetic state the structure of the *s*-, *p*-, and *d*-hybridized bands is spin dependent. In Figure 3 only the contributions of the 3*d* and 4*s* bands are depicted. The wave functions that correspond to the energy states exhibit *d* structure character and only a little admixture of *s* character.

The total charge within the unit cell was determined by adding the charge of the Fe atoms and the interstitial charge. This charge was found to be 52.006 a.u., corresponding to a neutral charge on the unit cell.

The constant muffin-tin potential between the spheres was found to be −0.762 Ry (spin down) and −0.714 Ry (spin up). Indicating the highest occupied state as the Fermi state, the corresponding Fermi energy is −0.571 Ry.

B. ⟨100⟩ Edge Dislocation in Fe

The cluster containing nine Fe atoms involved in the electronic structure calculation is indicated in Figure 2. The symmetry properties of the dislocated system obey the C_{2v} symmetry group. Figure 4 illustrates the sequences of the orbital energies belonging to the various representations. No marked influence was observed of the *p* states during the self-consistent calculation. Only the energy states that exhibit *ds*-structure character are shown in Figure 4. The

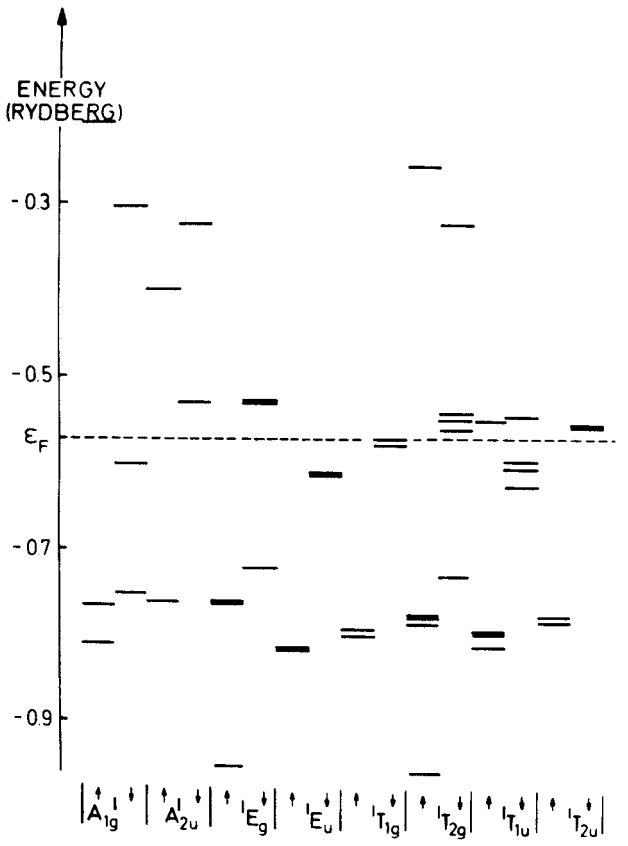

Figure 3. Energy levels of (spin polarized) α-Fe.

corresponding wave functions possess pronounced d character. The highest occupied orbital state corresponds to a Fermi energy of -0.578 Ry.

4. Discussion

The redistribution of the electrons around an edge dislocation is evident from a comparison between Figures 3 and 4. In the perfect lattice 72 electrons are distributed over 30 energy states within a range of about 0.38 Ry. The calculation for a dislocation shows that 72 electrons are distributed over 72 energy levels within a range of 0.42 Ry below the Fermi level. When one approaches a line defect from far away in the perfect region of Fe, the number of occupied energy levels are distributed over the irreducible representations of the O_h symmetry group, according to (spin polarized):

$$\Gamma = 3A_{1g} + 2A_{2u} + 3E_g + 2E_u + 2T_{1g} + 4T_{1u} + 5T_{2g} + 2T_{2u}. \quad (1)$$

The greater number in energy levels in the dislocated lattice is caused by the

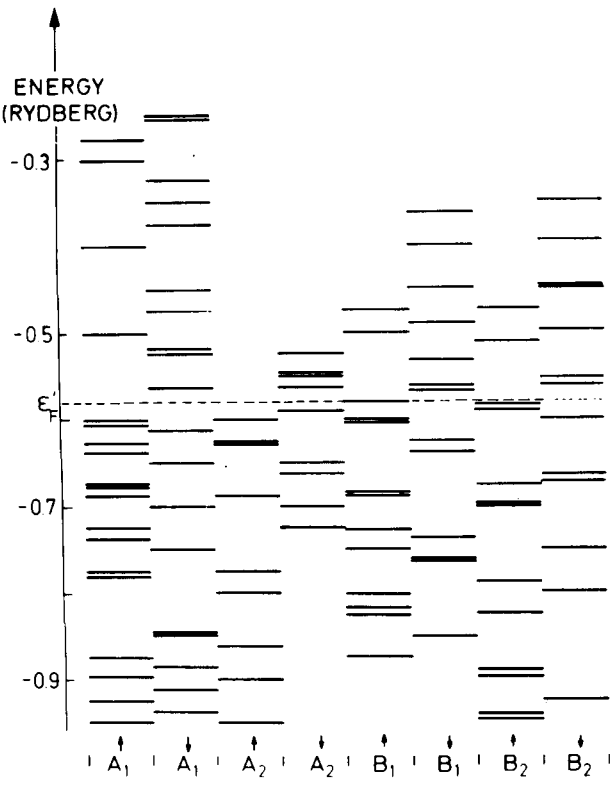

Figure 4. Orbital energies calculated for a ⟨100⟩ edge dislocation in α-Fe.

reduction in symmetry going from perfect cubic symmetry O_h to the symmetry properties of the C_{2v} group. By the decrease in symmetry the distribution of the electrons over the irreducible representation becomes

$$\Gamma = 19A_1 + 9A_2 + 13B_1 + 13B_2. \tag{2}$$

The highest occupied orbital in the case of the dislocated lattice (ϵ_F') is lower than for the perfect lattice. However, the Fermi states have to be equal. This may be explained as follows: suppose that the perturbation potential is δV relative to the perfect lattice where the Fermi energy state is ϵ_F. The Fermi distribution of the electrons will then be lifted or lowered by the amount δV relative to the distribution in the perfect lattice where δV has to be equal to zero. But that either means that ϵ_F changes to ϵ_F' or that an electron flow occurs around the dislocation core region. Of course, the latter must happen because ϵ_F must be a constant throughout the whole volume. The Fermi states ϵ_F and ϵ_F' can be equalized by either introducing a charge of +0.01 on the Watson sphere or by increasing the occupation number of the Fermi level in the case of the dislocated lattice. This small change in electronic occupation may be considered as a change resulting from an electron density distribution around the defect. In the case of an edge

dislocation the electrical neutrality cannot be determined in the same way as in the case of the perfect lattice by counting the charges on the atomic spheres and the interstitial spaces because of the lack of a unit cell.

One knows that in a metal the cloud of conduction electrons takes energies within two limits ϵ_0 and ϵ_F, according to the Pauli principle. This cloud will vary with the dilatation Δ of the lattice. Neglecting the interaction of the inner atomic shells it is evident that the stability of the metal requires the average energy ϵ_F to be stationary with respect to Δ. The electron density in the core region of the edge dislocation calculated is higher at the dilatational side than at the compression side of the dislocation. It means that electrons tend to flow away from the compression side toward the dilated regions. For an edge dislocation in Fe the shift of electrons is toward the expanded side and away from the half plane. This is illustrated in Figure 5. The dilatation is greatest in the region within one atomic spacing of the edge of the half plane. According to the values for ϵ_F and ϵ_F', it means that the electrical contribution to the binding energy of a solute atom and a dislocation in α-Fe is of the order of 0.01 Ry/electronic unit of charge on the atom. It is noteworthy that the elastic binding energy of impurities in α-Fe is about eight times greater than the electrical one. It appears that in Fe-based alloys the role of the electrical interaction is secondary to that of elastic interaction [12,13].

Nevertheless, the cluster method takes into account more correctly the atomic positions within the core region than other methods do and it provides more detailed information about the electronic states connected with a dislocation.

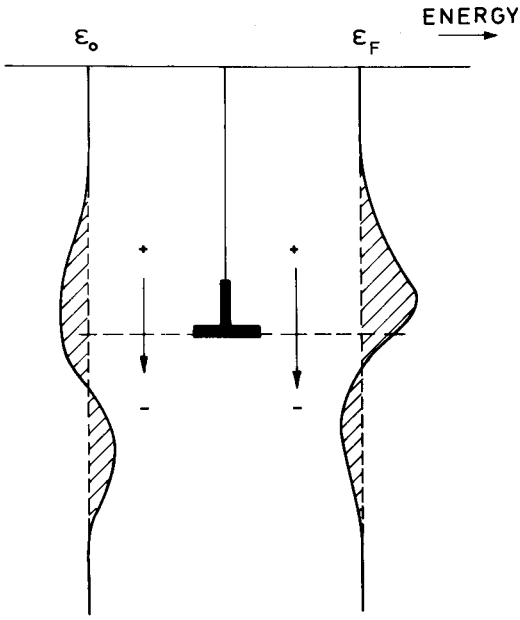

Figure 5. Schematic representation of an electric dipole produced in a metal by an edge dislocation. ϵ_0 and ϵ_F represent the bottom and top of the energy band, respectively.

In that way it provides a possible procedure to investigate the as yet unknown effects of electronic structure on phenomena such as the segregation of impurities near dislocations, Peierls barriers which play an important role in problems derived from materials science and technology.

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